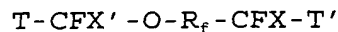


## CLAIMS

1. A process for the preparation of perfluoropolyethers of

formula:



(I)

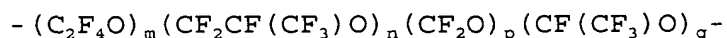
wherein:

T is -F, C<sub>1</sub>-C<sub>3</sub> perfluoroalkyl, -CH<sub>2</sub>OH, -CH<sub>2</sub>NH<sub>2</sub>, -CHO;

T' = T with the proviso that when T is F or C<sub>1</sub>-C<sub>3</sub> perfluoroalkyl, T' is -CH<sub>2</sub>OH, -CH<sub>2</sub>NH<sub>2</sub>, -CHO;

X, X', equal to or different from each other, are -F or -CF<sub>3</sub>;

R<sub>f</sub> is selected from:



wherein the sum n+m+p+q ranges from 2 to 200,

the (p+q)/(m+n+p+q) ratio is lower than or equal to

10:100, preferably comprised between 0.5:100 and 4:100,

the n/m ratio ranges from 0.2 to 6, preferably from 0.5

to 3; m, n, p, q are equal to or different from each

other and when m, n range from 1 to 100, preferably from

1 to 80, then p, q range from 0 to 80, preferably from 0

to 50; the units with n, m, p, q indexes being

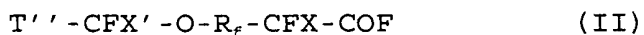
statistically distributed along the chain;

-(CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>O)<sub>r</sub>- wherein r ranges from 2 to 200,

-(CF(CF<sub>3</sub>)CF<sub>2</sub>O)<sub>s</sub>- wherein s ranges from 2 to 200,

comprising the following steps:

- A) preparation of perfluoropolyethers of formula



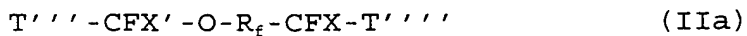
wherein  $T''$  is  $-COF$ ,  $-F$ ,  $C_1-C_3$  perfluoroalkyl,  $X$ ,  $X'$ ,  $R_f$  are as above, by reduction of the corresponding perfluoropolyethers containing peroxidic bonds, with gaseous hydrogen in the presence of a catalyst formed by metals of the VIII group supported on metal fluorides, at a temperature from  $20^\circ C$  to  $140^\circ C$ , and at a pressure between 1 and 50 atm;

- B) treatment of the formula (II) compounds with inorganic chlorides, preferably  $CaCl_2$ , by heating at a temperature in the range  $100^\circ-150^\circ C$  obtaining perfluoropolyethers having acylchloride  $-COCl$  end groups;

- B') treatment of the formula (II) acylfluoride or of the corresponding ester or of the corresponding acylchloride with gaseous ammonia, obtaining the corresponding amide, subsequently dehydrated preferably with  $P_2O_5$ , at a temperature in the range  $150^\circ-200^\circ C$ , preferably at  $170^\circ C$ , with the obtainment of perfluoropolyethers with nitrile  $-CN$  end groups;

- C) reduction of the perfluoropolyethers with acylchloride end groups, obtained in step B), or with nitrile end groups, obtained in step B'), of formula

(IIa):



wherein:

 $T'''' = -F, C_1-C_3 \text{ perfluoroalkyl}, -CN, -COCl,$ 
 $T''''' = T'''' \text{ with the proviso that when } T'''' \text{ is } -F \text{ or}$ 
 $C_1-C_3 \text{ perfluoroalkyl}, T''''' \text{ is } -CN, -COCl,$ 

with gaseous hydrogen in the presence of a catalyst constituted by metals of the VIII group selected from Pd, Rh, Ru, supported on solid metal fluorides, at a temperature from 20°C to 150°C, preferably from 80°C to 120°C and at a pressure between 1 and 50 atm, preferably between 1 and 10 atm, optionally in the presence of inert solvents.

2. A process according to claim 1, wherein  $R_f$  is selected from the following structures:  
 $-(CF_2CF_2O)_m-(CF_2O)_p-$ ,  
 $-(CF_2CF(CF_3)O)_n-(CF_2O)_p-(CF(CF_3)O)_q$ .
3. A process according to claims 1-2, wherein the metal fluoride of step C) is selected from the group formed by  $CaF_2$ ,  $BaF_2$ ,  $MgF_2$ ,  $AlF_3$ , preferably  $CaF_2$ .
4. A process according to claims 1-3, wherein the concentration of the VIII group metal on the metal fluoride of the catalyst of step C) is comprised between 0.1% and 10% with respect to the total weight of the catalyst, prefe-

rably between 1% and 2% by weight.